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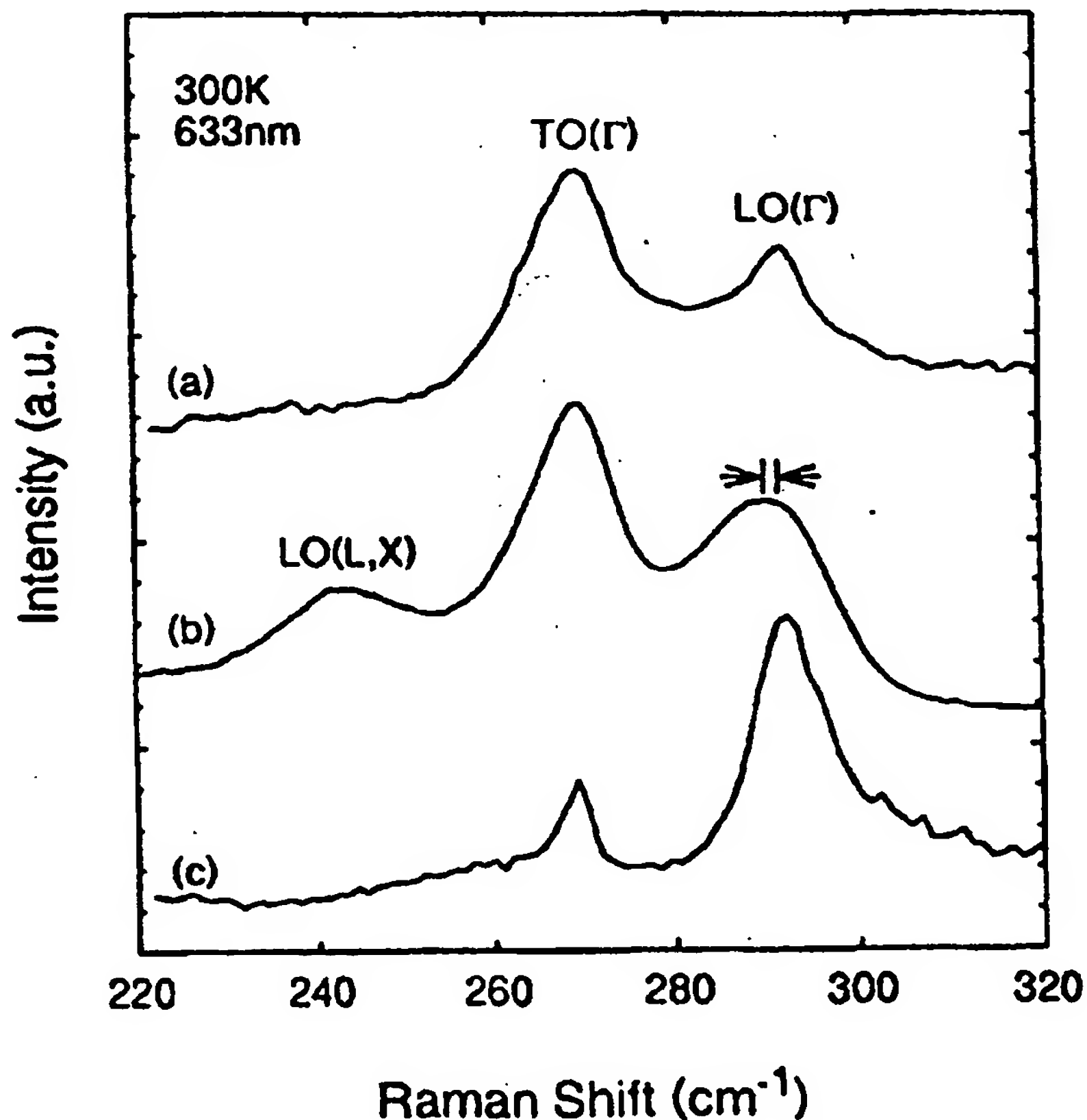
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(54) Title: RAMAN SPECTROSCOPIC ANALYSIS OF DAMAGES IN SEMICONDUCTORS

(57) Abstract

III-V semiconductor dot samples (particularly GaAs) have been studied with Raman microscopy. The samples were fabricated by electron beam lithography and dry etching. The non-resonant Raman scattering can provide direct information on the structure alteration and associated phonon bands. In particular, a previously unknown Raman line at 242cm^{-1} is attributed to a non-allowed phonon caused by damage. Direct Raman imaging in this band can reveal the damaged portions of the sample.



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Raman spectroscopic analysis of damages in semiconductors.

Field of the Invention

5 This invention relates to analysing a sample using Raman spectroscopy. More particularly, it relates to analysing surface or sub-surface damage in a sample.

Description of the Prior Art

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It is known that damage in semiconductors such as GaAs can be investigated by studying Raman scattering. See for example, P.D. Wang et al, Journal of Applied Physics, volume 71, number 8, page 3754 (1992).

15

A Raman analysis apparatus is available commercially from the present applicants Renishaw plc. It can be used in a microscope mode, in which a two-dimensional image of the sample is viewed in Raman scattered light of a selected wavenumber on a charge coupled device (CCD).

20

Alternatively, it can be used in microprobe mode, in which a point on the sample is illuminated, and a spectrum of Raman scattered light from that point is analysed. Various aspects of this commercially available system are described in U.S. Patent No. 5,194,912, European Patent Application No. 0543578 and International Patent Application No.1 WO92/22793. These specifications are incorporated herein by reference, and the reader should refer to them for further details.

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Summary of the Invention

The present invention arose as a result of work carried out using the above Raman system. III-V semiconductor dot samples were fabricated by electron beam lithography and dry etching, and the non-resonant Raman scattering from the sample was analysed. This provides direct information on the structure alteration and associated phonon bands.

35

Direct two-dimensional imaging in selected Raman bands reveals the uniformity of the micrometer-sized dot arrays. The sample may, for example, be of GaAs or GaAlAs.

- 5 With such materials, two phonon peaks are observed at approximately 269 and 292cm^{-1} . However, we have now discovered various previously un-observed effects, attributed to surface damage during the fabrication process. One such effect, for example, is the presence of
- 10 an additional peak at about 240 to 242cm^{-1} . This is believed to be caused by a non-allowed phonon (that is, a phonon which would not be allowed if the structure of the sample were perfect).
- 15 The present invention therefore provides a method of analysing surface or sub-surface damage in a sample, by illuminating the sample and analysing the Raman scattered light which it produces. Analysis is made particularly of the newly-discovered effects mentioned above. One
- 20 particularly preferred analysis method, for III-V semiconductor samples such as GaAs, is to form a two-dimensional image of the sample in Raman scattered light in the non-allowed phonon band. The resulting image highlights those parts of the semiconductor which have been
- 25 most damaged.

In addition to III-V semiconductor samples which may have been damaged during electron beam lithography and dry etching, the invention can also be used to assess damage

30 caused during other machining processes. Examples include high precision diamond turning, polishing, grinding, abrasion, other physical machining, laser ablation, wet etching, ion-beam milling, plasma etching, etc.

- 35 Other Raman analysis systems can be used in the present invention, but the Renishaw system is preferred because it has a much higher optical throughput. This means that thin

layers can be analysed, even monomolecular layers, in materials which are not highly Raman sensitive.

Brief Description of the Drawings

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Preferred embodiments of the invention will be described with reference to the accompanying drawings, wherein:

Fig 1 is a graph showing Raman spectra, the intensity in arbitrary units (a.u.) being plotted against the Raman shift in cm^{-1} ;

Figs 2(a) and 2(b) are Raman microscope images of the sample, taken in the 269cm^{-1} band shown in Fig 1;

Fig 3 is a surface intensity plot computed from the data which produced Fig 2(b);

Fig 4 is a further Raman spectrum; and

Fig 5 is a schematic diagram of Raman apparatus used to produce these spectra and images.

20 Description of Preferred Embodiments

A Renishaw Raman imaging microscope (Ramascope) is shown schematically in Fig 5. Fuller details of the apparatus are given in EP 0543578 and W092/22793, and the various features discussed in those specifications may be incorporated in the present apparatus. Briefly, an incoming laser beam 10 is directed by a dichroic filter 12 through a microscope objective 16 and focused at 19 on a sample 18. Raman scattered light from the sample passes back through the microscope objective 16 and through the filter 12, which rejects light having the same frequency as the incoming laser beam 10, e.g. Rayleigh scattering. The Raman scattered light then passes to a Raman analyser 20 and is focused by a lens 22 onto a cooled charge coupled device (CCD) detector 24. The data from the CCD is acquired and analysed by a computer 25.

The Raman analyser 20 may be based upon a diffraction grating, which disperses a Raman spectrum across the CCD 24, as indicated at 28. Alternatively, this may be swapped for a non-dispersive tunable filter. In this case, it is possible to defocus the incoming laser beam 10 so as to illuminate an area on the sample 18. A two-dimensional image of this illuminated area is then produced on the CCD 24, in light of the wavenumber selected by the tunable filter in the analyser 20.

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Confocal action of the microscope may be achieved by a spatial filter 14 between the dichroic filter 12 and the microscope objective 16, or in any of the other ways described in W092/22793.

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Raman spectroscopy is a well established experimental technique for the characterisation of semiconductors¹. In addition to studies of bulk material, structures on the scale of 1 μm can readily be investigated by Raman microprobe spectroscopy². This technique provides non-destructive and quantitative microanalysis of semiconductor structures and their electrical properties³.

In Raman microprobe spectroscopy an optical microscope is used to focus the laser onto the specimen and collect the Raman scattered light for analysis by a spectrometer. Spatial information can only be obtained by a Raman mapping procedure in which the focus spot is moved stepwise over the two dimensional (2D) surface of the sample⁴. In Raman microscopy (or Raman spectroscopic imaging) a microscope is also used to deliver the laser light to the specimen and collect the Raman scattered light. In this case, however, the laser is used to illuminate an area on the specimen and the Raman scattered light used to form the image is selected by a narrow band filter^{5,6}. In this way it is possible to obtain a two dimensional image showing the location of the material that gave rise to the particular Raman band.

In the present experiments a Renishaw Raman Imaging Microscope (Ramascope) has been used to study an array of GaAs dots which have diameters close to 1 μm . In the microprobe mode the grating section of the instrument gives a spectral resolution of better than 2 cm^{-1} for Raman shifts from 50-4000 cm^{-1} . The confocal nature of the instrument limits the scattering volume in the specimen to a cylinder of approximately 1 μm in diameter and 2 μm in height when a microscope objective of numerical aperture (NA) greater than 0.8 is used. In the Raman imaging mode the instrument has a spectral resolution of 20 cm^{-1} ; this is determined by the narrow-band multilayer filter used to select the Raman band. Different Raman bands may be selected for imaging by rotating the filter with respect to the optic axis. The high quality of the bandpass filter causes no disturbance at all, so that the spatial resolution of the Raman image is only limited by the optical microscope and the

matching to the multi-channel detector. The Ramascope is able to record 2D images across an area of 100 μm in diameter with the resolution close to 1 μm .

Raman microscopy has important advantages in the microanalysis of semiconductor materials and devices. A typical device element in current VLSI (very large scale integration) technology is about 1 μm , which is compatible with the spatial resolution of the Raman microscope using visible light. As-grown and device characterisation includes a) damage induced by ion implantation⁷ or dry etching which will be discussed later in this paper, b) strain mapping of the surface⁸, c) crystallographic orientation by Raman polarization studies⁹ and d) free carrier concentration in zinc-blende solids by plasmon-longitudinal optical (LO) phonon coupling¹⁰. Recent resonant Raman scattering by using a Raman microscope revealed confined phonons and their anisotropy in semiconductor quantum wells¹¹. In this paper we report a micro-Raman study of GaAs dot arrays of diameter close to 1 μm . A Raman image has been obtained for such microstructures. The dot array structural uniformity and damage will be discussed.

The GaAs sample was defined by electron beam lithography and subsequently etched by SiCl_4 reactive ion etching (RIE). The fabrication details have been reported elsewhere¹². Raman spectra and images were recorded with a 25 mW and 633 nm line emission He-Ne laser. Fig.1 shows three typical Raman spectra obtained from a 1.36 μm dot sample. In the spectral mode, the sample illumination has a point-focus to provide the highest possible resolution. A typical integration time is 60 sec. Fig.1(a) is the Raman scattering spectrum obtained from the dot area (usually contains 1 or 2 dots). The two main peaks are GaAs LO and transverse optical (TO) phonons, at 292 and 269 cm^{-1} , respectively. The TO phonon is usually forbidden for (100) surface backscattering. However, it is observed because the non-planar surface is patterned with dots which induce random scattering and cause a breakdown of the selection rules. It is also due to the large collection angle employed by the Ramascope. Fig.1(b) is also from another dot area of the sample. In addition to the two main peaks, a third peak (242 cm^{-1}) is observed which is

associated with the Brillouin zone edge LO phonon modes (L or X). The observation of this band is attributed to the structural damage of that particular dot. The breakdown of momentum conservation induces the zone-edge phonon mode in the first order Raman scattering. Furthermore, the LO phonon band in Fig.1(b) is also slightly shifted towards the lower energy with asymmetric broadening. This indicates that the phonon coherence length L_c has been reduced¹³. Structural damage breaks the translational symmetry of the crystal, thus the phonon will no longer perceive an infinite crystal and its spatial correlation will become finite in extent which in turn increases the phonon wave vector uncertainty δk . From Fig.1(b), L_c is estimated to be 25 nm. Such a relatively large value of L_c implies that the sample has suffered a low level of damage. Fig.1(c) is a spectrum of the substrate area surrounding the base of the dot. The etched surface shows a very small signal of the TO phonon and approximately symmetric LO phonon line. By moving the sample, it is found that most of the dot areas yield a Raman spectrum similar to Fig.1(a). Conventional Raman spectroscopy has been used before to characterise the dry etch damage¹⁴. Doped material was used to study the surface damage in order to produce a quantitative comparison between different dry etching techniques by investigating the plasmon-LO phonon coupling strength. In the Raman microscopy, within the resolution limit, single dot characterisation is possible and can reveal directly the dry etch induced damage. This damage is not necessarily physical but can affect the optical and electrical properties of potential quantum dot devices. Cathodoluminescence has been studied in a previous investigation of GaAs-AlGaAs quantum well dots and revealed that even the physically intact quantum dots did not luminesce^{15,16}. Here, in principle, we can adapt a Raman microscope to probe the emission of the quantum dot and correlate the luminescence intensity with the Raman signal.

The intensity contrast of the TO phonon peak between the dot and its surrounding area provides the basis for the Raman imaging which is shown in Fig.2 and Fig.3. To reduce the background scattering light, an image centred at 200 cm^{-1} has also been taken to

assist the data processing. Fig.2(a) shows the 269 cm^{-1} band image with band width of 20 cm^{-1} . The background level measured at 200 cm^{-1} has been subtracted ($I(269\text{ cm}^{-1}) - I_0(200\text{ cm}^{-1})$). Fig.2(b) shows the same image but flat-fielded by the same 200 cm^{-1} background to eliminate the effect of uneven illumination, i.e. $[I(269\text{ cm}^{-1}) - I_0(200\text{ cm}^{-1})]/I_0(200\text{ cm}^{-1})$. The $1.36\text{ }\mu\text{m}$ dots can be seen clearly in the Raman image. The bright area is mainly due to the TO phonon peak in the image with a significant LO phonon contribution. The uneven surface provides significant scattering of the light. The integration time is 200 sec, longer than point illumination in the Raman spectroscopy mode. Fig.2(a) provides a better imaging than Fig.2(b). Fig.3 shows a surface-intensity plot of Fig.2. It demonstrates directly the microscopic picture of the dot array. Fig.3 shows more of the Raman intensity variation on the dots. By studying these pictures we see the similarity from dot to dot and the large scale uniformity.

Fig.4 shows a Raman spectrum of 100 nm dots. The rather broad feature below the LO phonon line is due to surface phonons¹⁷. It was found that the surface phonon intensity increases dramatically with surface-to-bulk volume ratio, i.e., with decreasing dot sizes. The dotted line is the deconvolution of the overlapped LO and surface phonons. The experimental data were modelled with a Gaussian line profile with proper background subtraction. Further details about the surface phonon mode in semiconductor nanostructures will be reported elsewhere. Raman imaging of 100 nm diameter dots remains difficult due to the optical resolution limit in micro-Raman.

In conclusion, we have used the microRaman technique to reveal the Raman image of GaAs micro-sized dots. With non-resonant excitation, the structural damage has been studied and shown to be quite small in dots fabricated by low energy dry etching. The 242 cm^{-1} Raman line increases with both power and time in the dry etch process indicating large damage.

To show the extent and positioning of the damage in the sample, the images and/or the surface intensity plot shown in Figs 2 and 3 may be repeated in the non-allowed phonon band at 242cm^{-1} .

5

Summary of Figs 1-4

Fig 1. The Raman spectra of the dot region is shown in (a) and (b). Most of the region displays a spectrum of (a) while (b) displays some structure damage with a typical 242cm^{-1} peak. The LO phonon peak is also red-shifted indicating the decrease of phonon coherence length. (c) shows a typical spectrum of the substrate area.

15

Fig 2. The Raman imaging of quantum dots using the 269cm^{-1} band. This corresponds to the GaAs TO phonon. (a) is the dot image with 200cm^{-1} background level subtraction. (b) is the same Raman image but flat-fielded by the 200cm^{-1} background.

20

Fig 3. The surface intensity of plot of Fig 2(b). This image shows the microscopic uniformity of the dot system.

25

Fig 4. A Raman spectrum of 100nm dots. The broad peak labelled S_1 is the surface phonon line. Dotted lines underneath are the deconvolution of the LO and surface phonon mode. Typical half width at half maximum is 2cm^{-1} for the LO and TO phonons and 4cm^{-1} for the surface phonon mode.

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Reference:

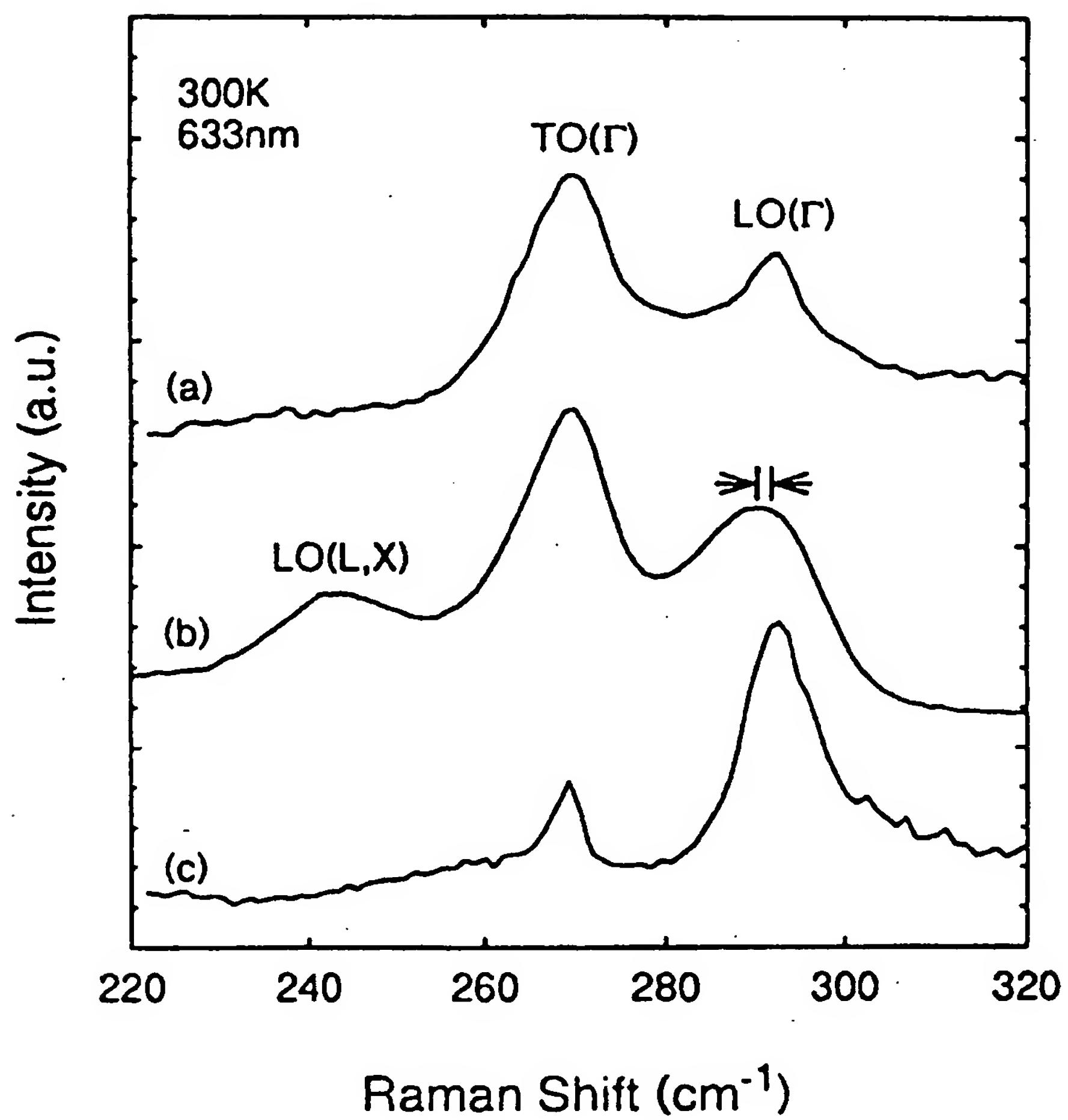
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CLAIMS

1. A method of analysing damage in a sample of a III-V semiconductor, comprising illuminating the sample and
5 collecting Raman scattered light from the sample;
characterised by analysing Raman scattered light in a band
which is due to non-allowed phonons caused by the damage.
2. A method according to claim 1, wherein said band of
10 Raman scattered light is associated with the Brillouin zone
edge LO phonon modes.
3. A method according to claim 1 or claim 2 wherein said
band is at a Raman shift of about 240cm^{-1} to 242cm^{-1} .
- 15 4. A method according to any one of the preceding claims,
in which an image is formed of an area of the sample, in
light of said band.
- 20 5. A method according to any one of claims 1-3, in which
an intensity plot is formed of an area of the sample, in
light of said band.
6. A method according to any one of the preceding claims,
25 in which the sample comprises GaAs or GaAlAs.
7. A method according to any one of claims 1-5, in which
the sample comprises GaAs.

Fig.1.



2/3

Fig.2.

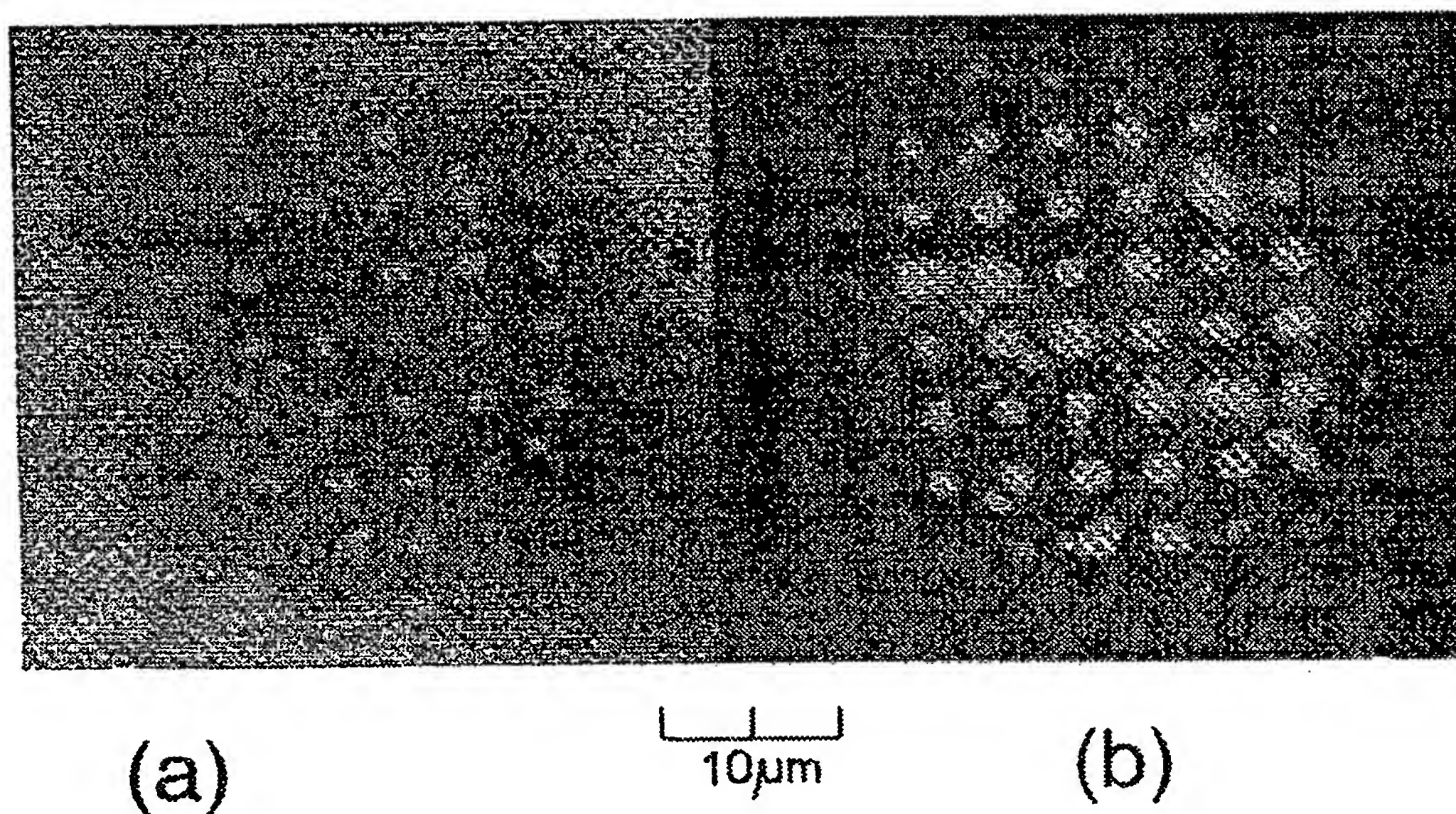


Fig.3.

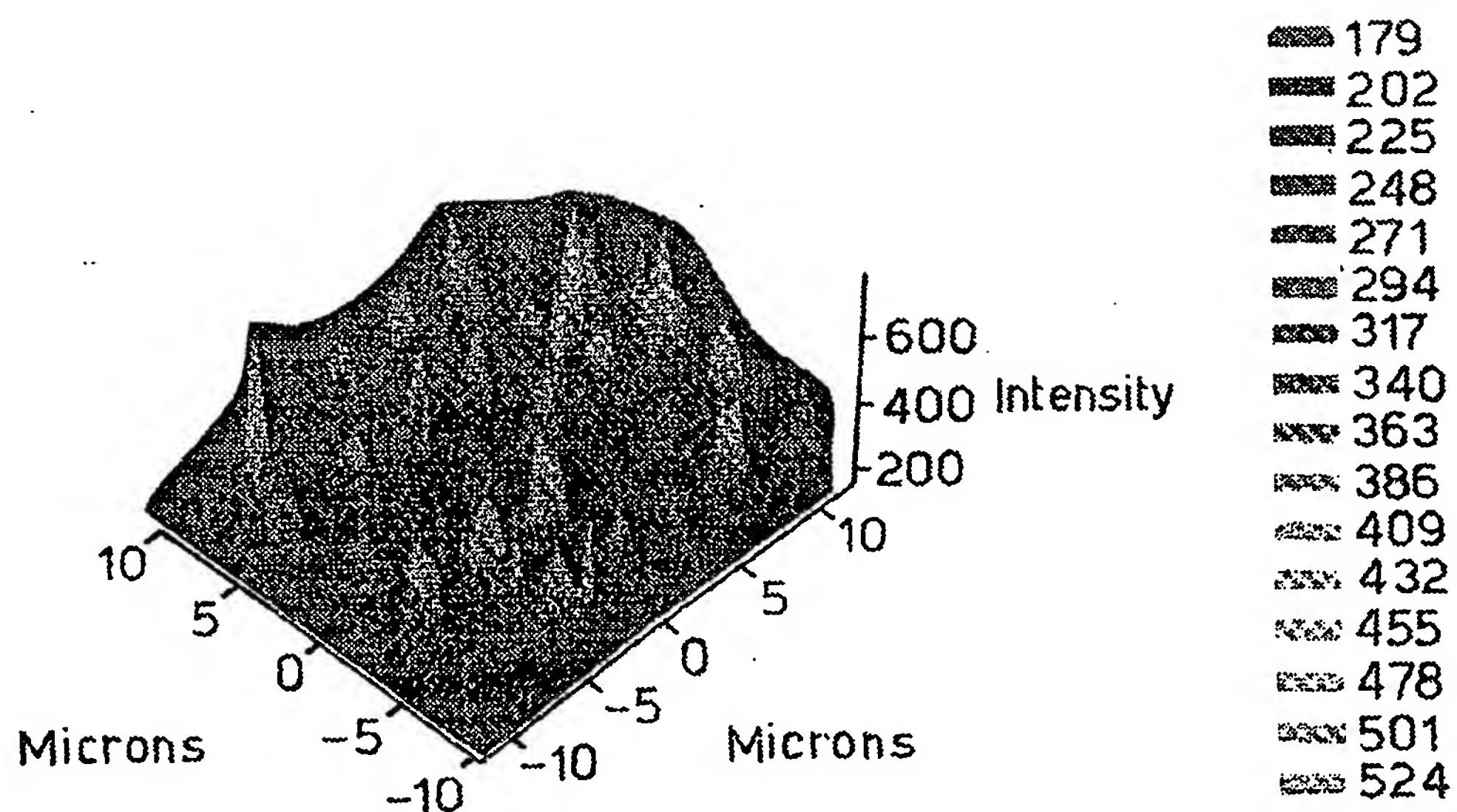


Fig.4.

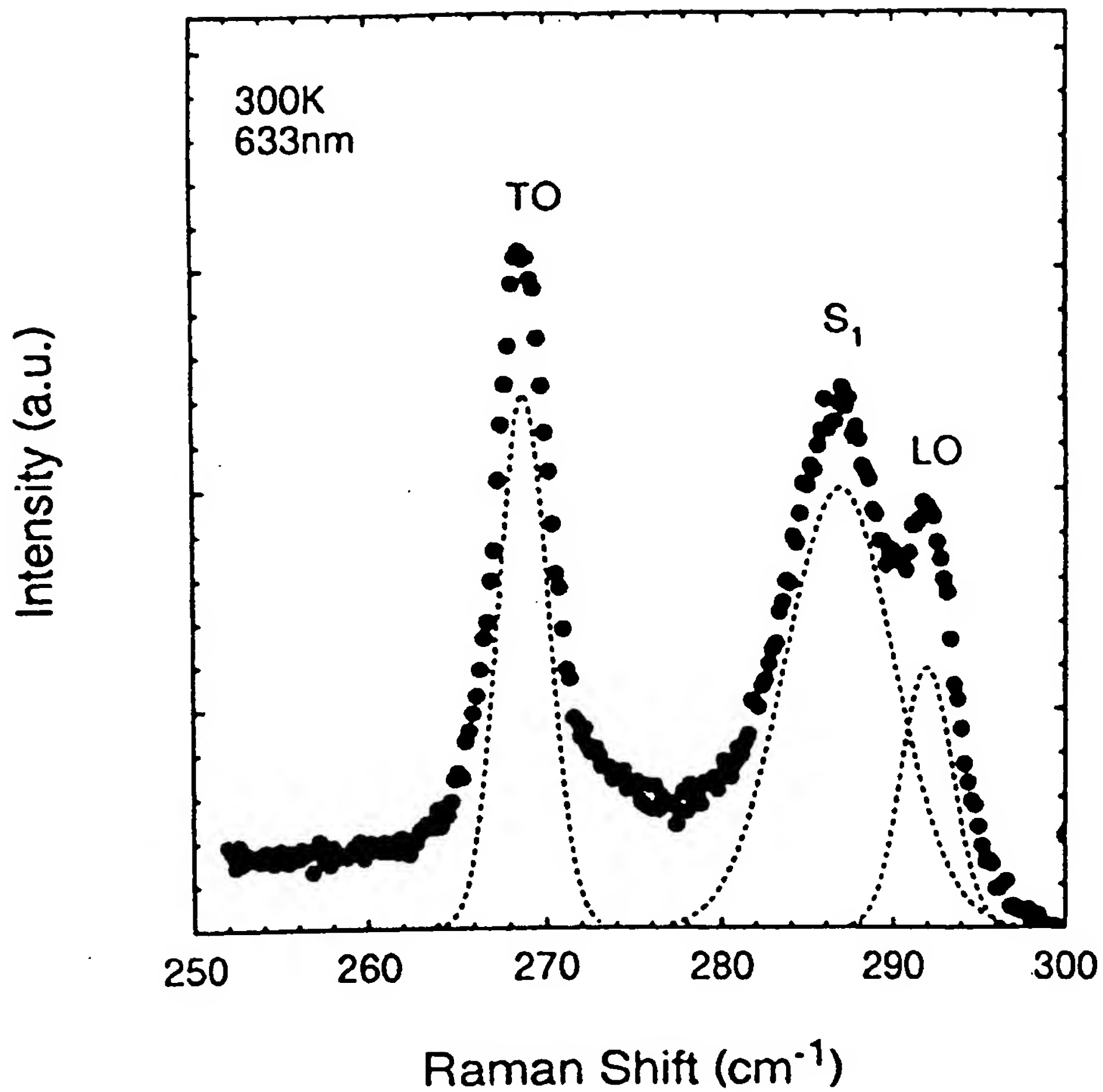
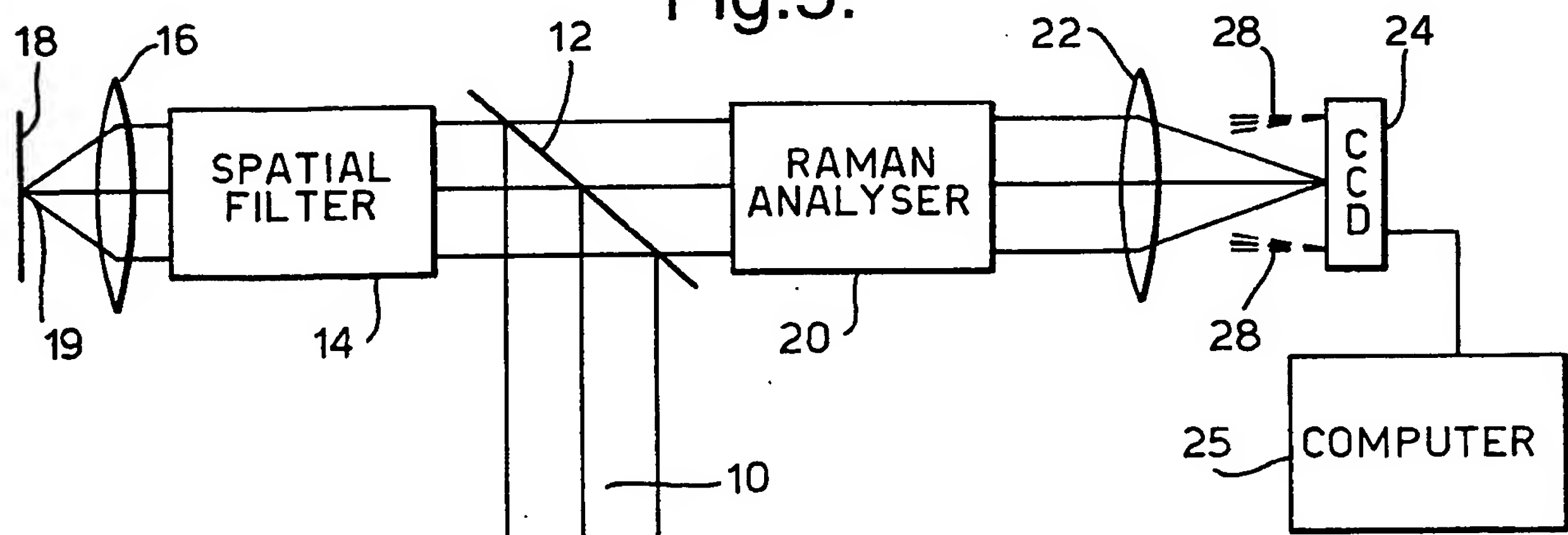


Fig.5.



INTERNATIONAL SEARCH REPORT

Interr. Application No
PCT/EP 94/02212

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N21/88 G01N33/44

According to International Patent Classification (IPC) or to both national classification and IPC

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 2 (P-532) (2449) 6 January 1987 & JP,A,61 181 945 (NEC) 14 August 1986 see abstract ---	1,4,6,7
A	PATENT ABSTRACTS OF JAPAN vol. 17, no. 209 (E-1355) (5838) 23 April 1993 & JP,A,04 348 521 (HITACHI) 3 December 1992 see abstract --- -/--	1,4,6,7

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	<p>PATENT ABSTRACTS OF JAPAN vol. 12, no. 224 (P-721) (3071) 25 June 1988 & JP,A,63 018 250 (KISO KAISEKI KENKYUSHO) 26 January 1988 see abstract -----</p>	1,4

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